THERMAL ANALYSIS CALORIMETRY

Applied to

THERMAL ENERGY STORAGE (TES)

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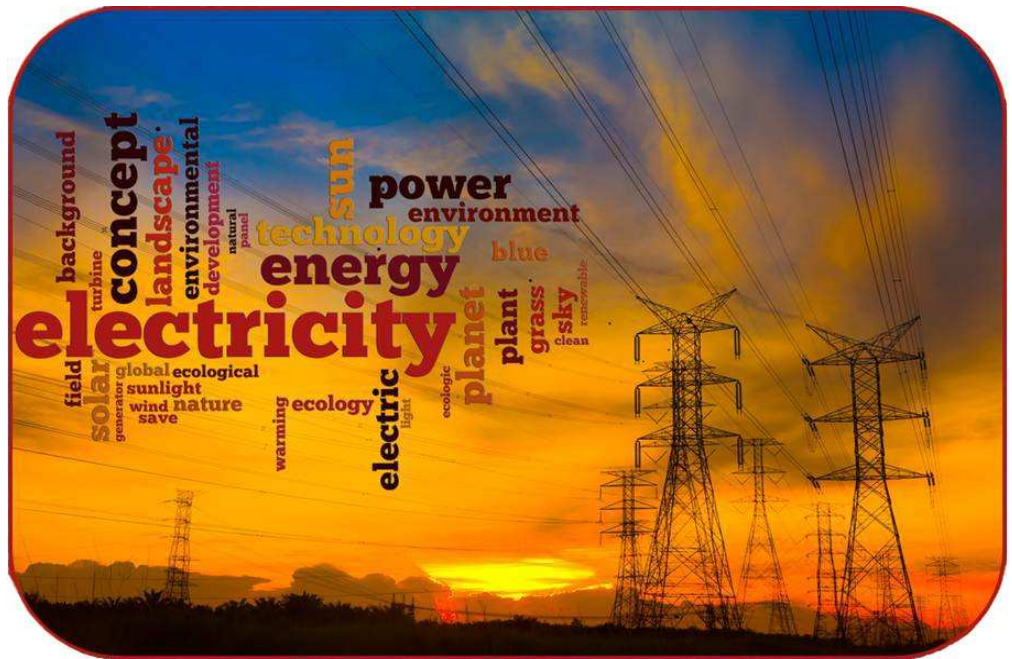
THERMAL ANALYSIS AND CALORIMETRY APPLIED TO THERMAL ENERGY STORAGE (TES)

Thermal Energy Storage (TES) is defined as the temporary storage of thermal energy. As most of the renewable energy sources (solar, wind, …) are only intermittently available, the target of TES is to improve performances of energy systems with a smoother supply and an increased reliability.

There are three main types of TES:
• Sensible heat
• Latent heat
• Thermochemical heat

This application update will demonstrate how the thermal analysis and calorimetric methods are used to investigate the different TES techniques and to characterize the materials (solid and liquid) used in the corresponding processes.
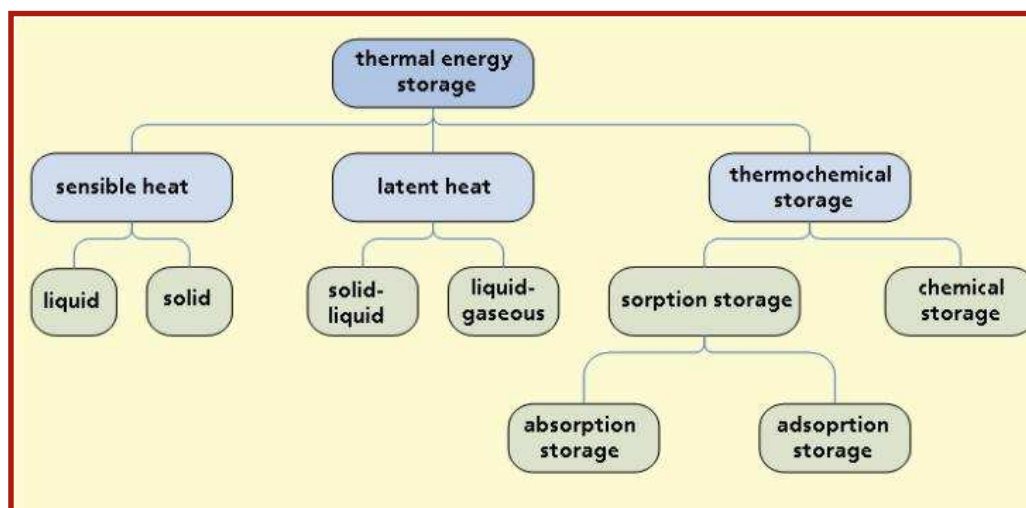
Presentation of the different Thermal Energy Storage (TES) modes
(from Fraunhofer IGB website)

Content

Latent heat storage with a blend of polyolefins encapsulated in polymer beads (MicroDSC)

Polyolefins encapsulated in polymer beads provide a further example of PCM. However, because of the nature of the sample it is not possible to get good data using a regular plate detector (see next example), and in this case a MicroDSC7 evo, equipped with a 3D Calvet type calorimetric sensor presented on Figure 1 provides a perfect solution.

The sample mass is 390 mg corresponding to about 10 beads. The sample is heated from -20 °C to 50 °C followed by cooling from 50 °C to -20 °C at 1 °C.min^{-1} and then at 0.04 °C.min^{-1} in order to measure the influence of the scanning rate on the hysteresis (Figure 2).
By lowering the scanning rate, the hysteresis is considerably reduced and sharper peaks of melting and crystallization are obtained.

The enthalpy variation of the tested PCM seen on Figure 3 clearly shows the influence of the scanning rate for the definition of the correct temperature range for an appropriated thermal energy storage.
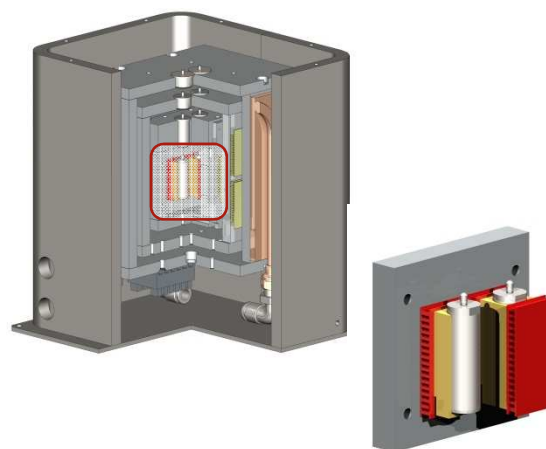

Figure 1
3D Calvet type calorimetric sensor of the μDSC7 evo

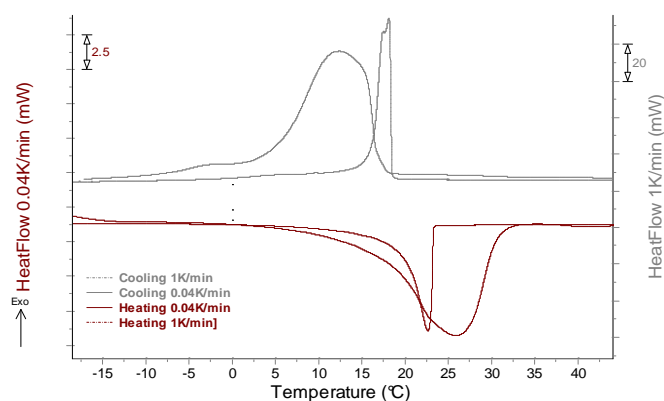*Figure 2*
Experimental DSC melting and crystallization profiles of the tested PCM at 0.04°C.min^{-1} and 1°C.min^{-1}
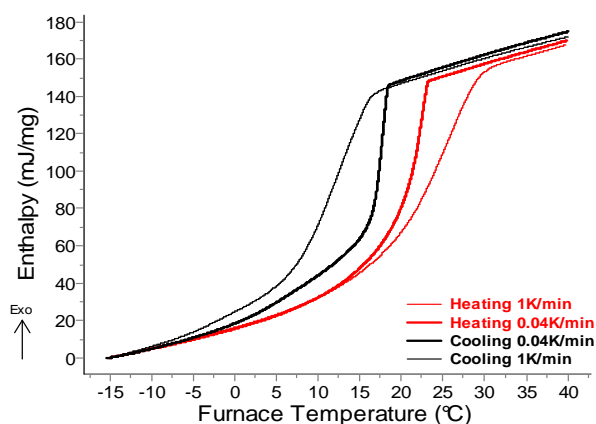

μDSC7 evo
- 45 °C to 120 °C

Figure 3
Enthalpy variations of the tested PCM during heating and cooling .

Latent heat storage with a plaster containing PCM (plate DSC)

One of the clearest illustrations of Phase Change Materials (PCM) is within plaster for building and specifically construction of walls.

The principle being that a phase change at a certain temperature will either adsorb or release energy allowing for controlled energy release within the construction.

An example is given with the investigation of a sample of plaster containing PCM. Approximately 50 mg of sample is analyzed with the DSC 131 evo, a standard plate DSC (Figure 5), into a closed aluminum crucible (100 µL) at a heating rate of 3 °C/min between -5 °C and 45 °C.

The material shows a very good melting/crystallization reversibility in term of temperature range and enthalpy (25.1 J.g^{-1}) that is perfectly adequate for its use as a TES substance (Figure 4).
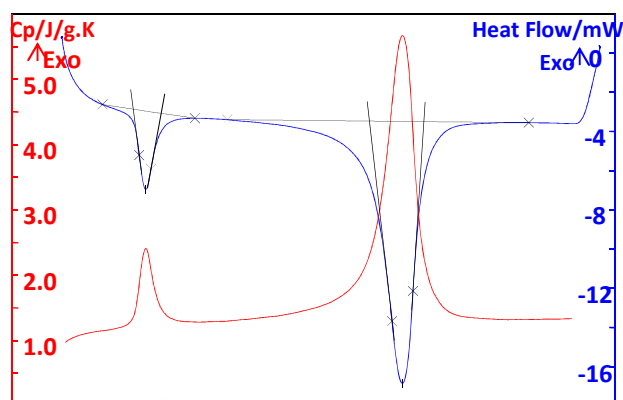

Figure 4
Melting and crystallization of a plaster containing PCM and cross-section of the DSC131 detector

Figure 5
Cross section of a standard plate DSC

DSC 131 evo
(-170°C / 700°C)

Latent heat storage with a large amount of hydrated salt (C80 calorimeter)

An example is given with the investigation of a mass of 10 grams of hydrated ferric chloride $FeCl_3,6H_2O$ at a low scanning rate (0.1°C.min^{-1}). The material is tightly encapsulated in a glass ampoule that is introduced in the calorimetric vessel. This encapsulation will prevent any evaporation or contamination between the sample and the metallic vessel. This operation is made possible due to the large volume of the experimental vessel.

The ferric chloride provides a large melting heat between 30 °C and 47 °C (Figure 6). The corresponding integral curve, including the heat capacity of the material and its melting enthalpy, provides the capacity of thermal energy storage for such a material

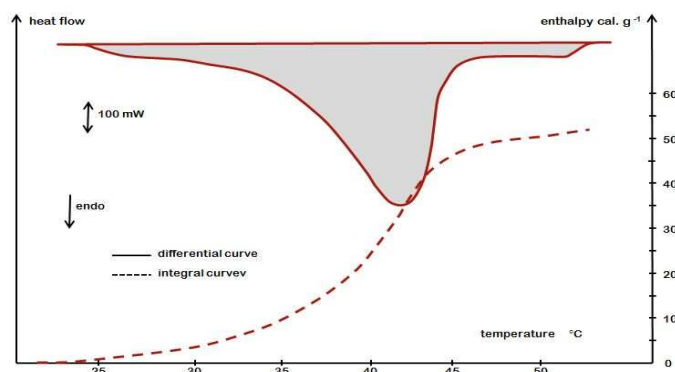*Figure 6*
Melting of hydrated ferric chloride (10.29 g) encapsulated in a glass ampoule at 0.1°C.min^{-1}

The C80 allows for the study of larger, more representative samples. The calorimetric detector is built with crowns of thermocouples that surround around the ensuring good integration of the heat exchange by the sample.

C80 Calorimeter – ambient to 300 °C

Formation and dissociation of CO_2 hydrates (High Pressure MicroDSC)

The formation and dissociation of CO_2 hydrates evolve a significant enthalpy value that is interesting for thermal energy storage. The formation of the hydrates requires a pressure of CO_2 around 20 bar and a low temperature.

A High Pressure vessel is used for such an experimentation (Figure 7). The vessel is connected to a high pressure gas panel to monitor the gas pressure and is introduced in the HP MicroDSC7 (Figure 8).For the test, water is introduced in the vessel and a pressure of 20 bar CO_2 is applied on the solution.

A sample of 269.51 mg of 10 wt% THF solution in water is cooled down to -20 °C to form the gas hydrate. Then the sample is reheated at 1 °C.min^{-1} to dissociate the hydrate. In the case of the formation of CO_2 hydrate, it is needed to firstly proceed to a cycling (successive heating and cooling) in order to obtain an hydrate accumulation.

The Figure 9 shows the decrease of the free water melting peak (0 to 10 °C) with the successive cycles and the appearance of a CO_2/THF co-hydrate melting peak (10 °C to 17.5 °C) and of the CO_2 hydrate melting peak (17.5 °C to 20 °C).

After 28 cycles (Figure 10), free water melting peak disappeared in favor of the co-clathrate and the hydrate dissociation.
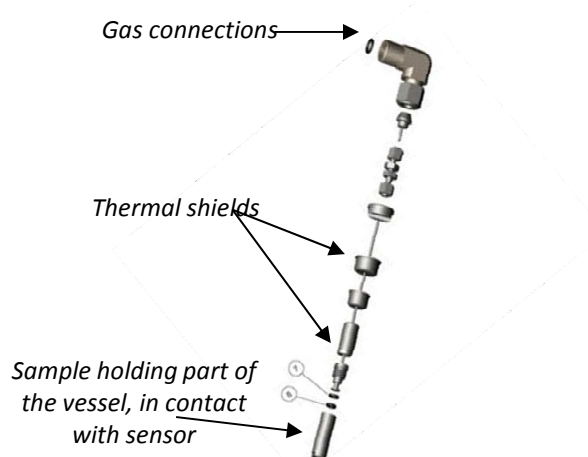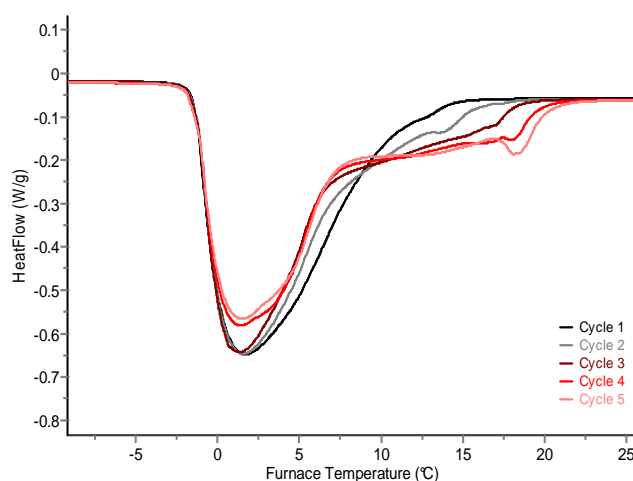

Figure 7
The High Pressure vessel

Figure 9
DSC thermograms recorded during successive cooling/heating cycles (1 to 5)

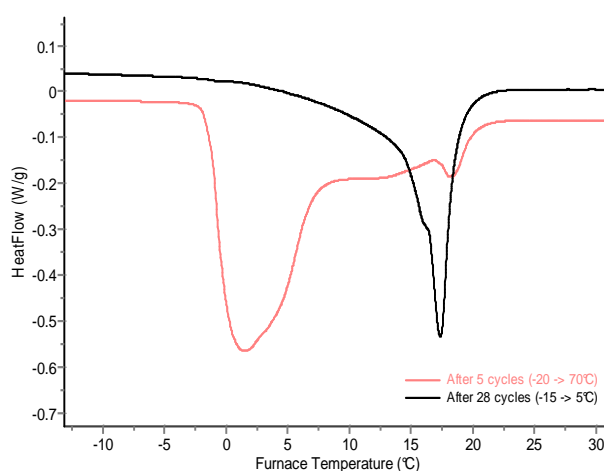*Figure 10*
DSC thermograms recorded during successive cooling/heating cycles (5 and 28)

Figure 8
Experimental setting for the investigation of gas hydrates

Formation and dissociation of CO_2 hydrates (High Pressure MicroDSC)

The cycle number 5 was used to perform a mathematical separation (Marquard routine fitting assymetric Gaussian peaks) on the three underlying peaks to have a clear separation of the contribution due to free water, the THF/CO_2 co-hydrate and the CO_2 hydrate (Figure 11).

From the peak separation it is possible to evaluate the heat of melting of the CO_2 hydrate that is equal to 12.18 J.g^{-1} of solution, i.e. 13.56 J.g^{-1} of water.

The comparison with litterature value of the heat of dissociation of CO_2 hydrate ($\Delta Hdiss$= 500,11 J.g^{-1} H_2O) allows determining a ratio of hydrate formation of 2.7% after 5 cycles. The same calculation can be applied to each cycle.
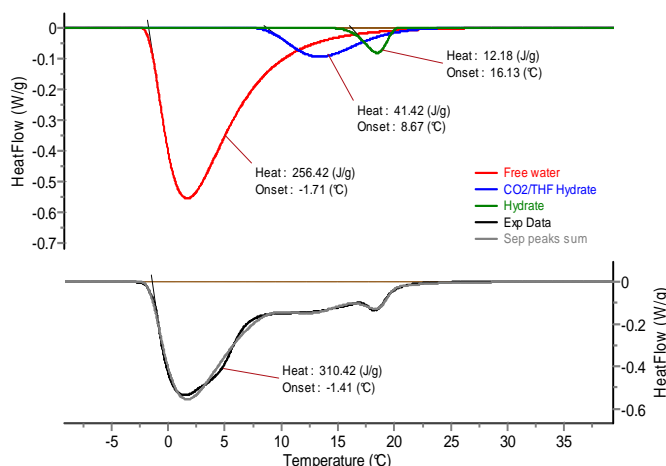

Figure 11
Separation of the thermal contributions of the melting of free water, CO_2/THF co-hydrate, and CO_2 hydrate for heating cycle 5

Adsorption of water on silica gel at different relative humidity (TG-DSC)

Using TG-DSC (Figure 13) it is possible to measure the capacity of adsorption (desorption) in term of mass and enthalpy on the same sorbent material.
An example is given with the sorption of water on silicagel at different relative humidity.
The following experimental conditions are selected:
▪ Silica gel initially activated by heating to 165°C to evacuate humidity
▪ Temperature of the adsorption test: 25 °C
▪ Sweeping of wet air (50 ml.min^{-1})
▪ 10 hours under different RH: 10%, 20%, 60% and 80%

The TG-DSC curves provide the mass increase due to water adsorption and the corresponding exothermic heat that define the heat storage capacity for such a material at a given temperature (Figure 14).
The interest of such a combined technique is that only one sample is needed to obtain both enthalpic and gravimetric information. This is especially important when the porosity of the material is a key factor in the adsorption process.

Figure 13
Sensys TG-DSC and Cross section of the Calvet DSC detector and the TG-DSC apparatus
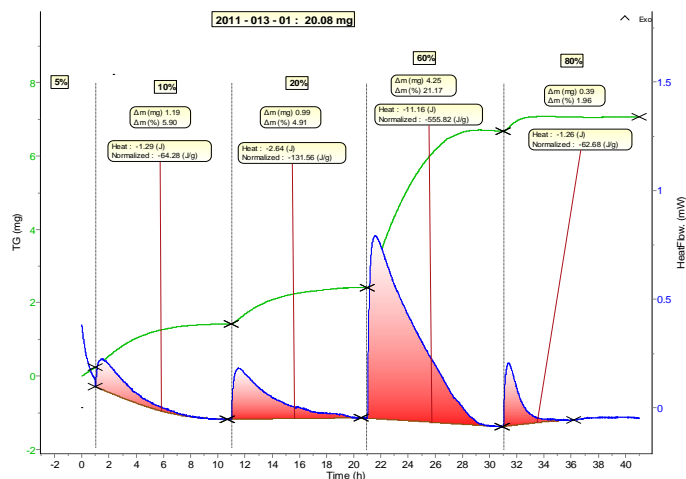

Figure 14
TG-DSC curves for the adsorption of water on silica gel at different RH

Adsorption of water on zeolite (C80 calorimeter)

Calorimetry is an important method for the investigation of the adsorption/desorption process. With the C80 , a gas flow vessel is available to introduce a vapour on a dry sample at a given temperature (Figure 15).

An example is given with the adsorption of water vapour on a zeolite at 24°C under different water vapour pressures (Figure 16).

The zeolite is initially activated during 6 hours at 312°C under vacuum. The gas flow calorimetric vessel, containing the activated zeolite,,is connected to a gas line coming from the water vapour generator. This generator is designed to work under reduced pressure of vapour. For the test, two vapour pressures are investigated: 4.58 mmHg and 9.20 mmHg.
The heat storage capacity is obtained versus the vapour pressure. According to the type of zeolite, this value can largely be different.
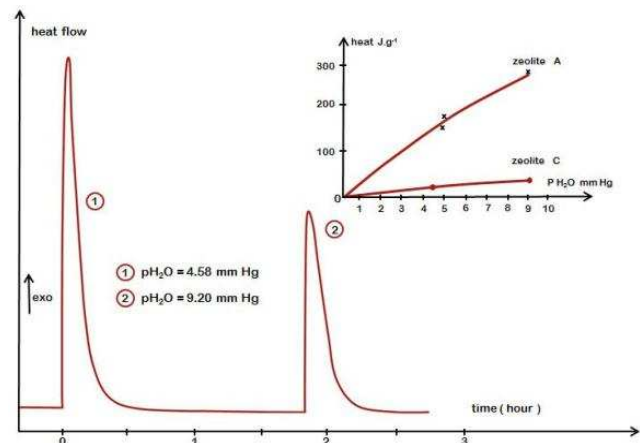

Figure 16
Water adsorption on a zeolite at different water vapour pressures at 24°C

Figure 15
Gas flow calorimetric vessel

Hydration of an attapulgite granulate (C80 calorimeter)

The same type of gas flow calorimetric vessel (Figure 15) is also very useful to follow the thermochemical heat storage relative to the sorption behavior of salt mixtures, and especially composites made of porous materials impregnated with hygroscopic salt hydrates. The exothermic reaction provide a high heat storage capacity. For the desorption process, a limited temperature up to 130 °C is only needed.

Figure 17 gives an example of the use of the gas flow vessel of the C80 calorimeter for the measurement of the hydration of an attapulgite granulate impregnated with different salt mixtures ($MgSO_4$, $MgCl_2$). The partial substitution of $MgSO_4$ by $MgCl_2$ results in a higher heat of adsorption
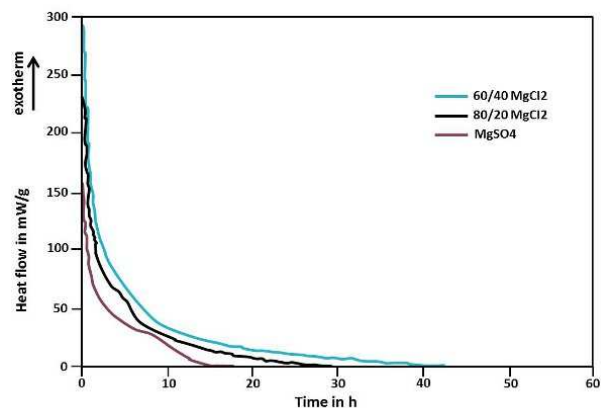

Figure 17
Hydration of attapulgite granulate impregnated with different salt mixtures at 30°C and 85%RH (from K. Posern and C. Kaps, Thermochimica Acta,502 (2010) 73-76)

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